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Hybrid thermoset matrix carbon fibre reinforced composites, a study of interlaminar properties

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Abstract. In this study carbon fibre reinforced epoxy, unsaturated polyester, and vinyl ester based, binary (two-component) hybrid matrix polymer composites were produced and mechanically characterized by interlaminar shear tests. Fracture surface of tested composites were investigated by scanning electron microscopy. Toughness of hybrid matrix composites were identified and compared to that of the reference, non-hybrid matrix ones.

Introduction

Researchers and developers intend to obtain favourable mechanical and thermal properties in case of polymer composites. Thermoset matrix polymer composites have great mechanical properties and relatively good thermal resistance, but they do not have as good toughness as the thermoplastic polymer ones, ductile metals, and alloys. High performance polymer composites usually have rigid reactions to quickly evolving and cyclic loads. Rigidity could be caused by rapid crack propagation and high fracture velocity inside the composite, mainly in the matrix and on the matrix-reinforcement phase boundary. This is the reason why it is important to improve toughness, without decreasing their great strength properties [1-5].

Usually, the matrix of the polymer composite is responsible for the toughness of the complete material. Toughness of thermoset resins can be improved in several ways. One of them is to create nanostructure by morphology modification of the material. On one hand, it is possible to incorporate nano-sized additives, nanoparticles into the resin, on the other hand there is an opportunity to interblend different types of resins. During the crosslinking process of different, mixed resins, the compound can be divided into at least two segments with the help of phase separation processes (binodal and spinodal decomposition). As a result of phase separation, in case of optimal conditions, it is possible that nanostructured hybrid resins are formed with co-continuous conformation. In this nanostructured material, the molecule chains of the components are rather entangled, hence lots of secondary bounds are formed . Additional flexibility and toughness may be achieved, as a result. Due to the above mentioned phenomena, crack propagation in hybrid resin is hindered by lots of bounds and molecule chain entanglements [1, 6-8].

If the above mentioned phase separated hybrid resin is used as the matrix material of a fibre reinforced composite (Fig. 1), the result can be improved damping properties, and enhanced toughness can be also reached. These hybrid resin matrix materials can be used in field of aircraft, automotive and sports equipment industries as well as high enegy absorbing structural material [6, 8, 9].

The main aim of our research work was to create nanostructured matrix high performance fibre reinforced polymer composites for engineering applications, and to investigate their morphological and mechanical properties.

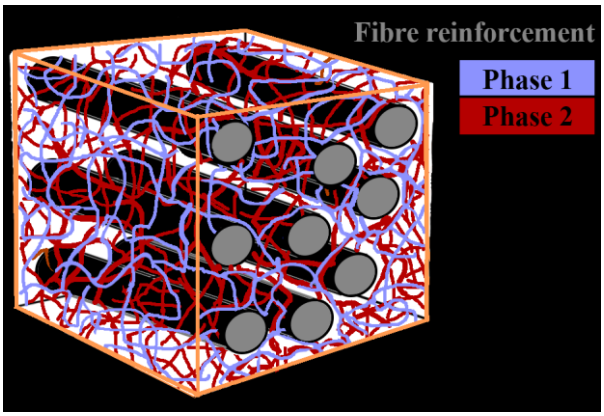

Figure 1 Theoretical structure of a co-continuous hybrid matrix fibre reinforced composite

Materials

As matrix material epoxy (EP), unsaturated polyester (UP), and vinyl ester (VE) were used. EP consisted of a bisphenol-A diglycidyl ether (with 188 g/epoxy equivalent, 12000 mPa·s viscosity at 25°C, and 1.17 g/cm^3 density, Ipox ER 1010 (product name), manufactured by Ipox Chemical Hungary) and isophorone diamine hardener (with 43 g/hydroxyl equivalent, 5-25 mPa·s viscosity at 25°C, ~660 mg KOH/g amine value, Ipox EH 2293 (product name), manufactured by Ipox Chemicals, Hungary). The UP resin was orthophthalic acid based (with 550-750 mPa·s Brookfield viscosity at 2 rpm at 20°C, 39-42% styrene content, DISTITRON 5119 ESX20ZQ (product name), manufactured by Polynt S.p.A., Argentina). The VE resin was a bisphenol based one, with 1300 mPa·s Brookfield viscosity at 5 rpm at 25°C, 35% styrene content, AME 6000 T 35 (product name), manufactured by Ashland Italia S.p.A., Italy. In case of VE and UP resins 2 wt% amount of methyl ethyl ketone peroxide accelerator was used (dissolved in diisobutyl phthalate), MEKP-LA-3 (product name), manufactured by Peroxide Chemicals, South Africa. As reinforcing material unidirectional, carbon fabric Panex 35 FB UD 300 (sized for epoxy)was used, manufactured by Zoltek Zrt., Hungary.

Experimental

Mixed resins were produced in two different ways. Two-component systems were created in 1:1 mixing ratio of EP/VE to EP/UP resins. In the first method (named ‘A’), EP and VE or UP resins were crosslinked simultaneously. In the first step of method ‘A’ resins were stirred for ten minutes. Then, the amine of EP was added and stirred for two further minutes. Finally, the catalyst of VE or UP was added and again stirred for two more minutes. In case of the second method (named ‘B’), components were crosslinked sequential-like mode. EP and its amine was mixed in stoichiometric ratio, and were stirred for two minutes. After that, it had 30 minutes rest time at room temperature without stirring. Then, the UP or VE was added and stirred calmly for two minutes. Finally, exactly the same way as in case of method ‘A’, the catalyst of the UP or VE was added and stirred for two more minutes. Composites were made by simple hand lay-up method using 6 unidirectional carbon fabric layers, the orientation of which were the same. After the hand lay-up, laminates were pressed between parallel steel plates in a hydraulic press with 0.5 MPa compressive stress at room temperature for 24 hours. Besides the EP/VE and EP/UP hybrid matrix, reference composites with the same reinforcement orientation and content were also prepared with neat EP, UP, and VE resin. After 24 hours of crosslinking at room temperature, all laminates were cured at 80°C for 4 hours. Test

specimens from the pressed laminates were cut in two different angles. One of them was parallel with (0°), another was perpendicular to (90°) the direction of fibre reinforcement.

Interlaminar shear strength (ILSS) tests of the composite materials were carried out in compressive mode at 1.3 mm/min test speed on a Zwick Z020 (Germany) universal testing machine at room temperature according to ASTM D3846-94, at least five different specimens in case of each composite types. The specimens of the ILSS investigation were double-side notched to the middle layer of the composite plates. Interlaminar shear strength (τ) values were calculated by dividing the maximal force during the compressive investigation with the area of the inner, non-notched cross section of the specimens. To avoid buckling, a special adapter was used during ILSS tests. Scanning electron micrographs (SEM) were taken by a JEOL JSM-6380 LA device. SEM samples were coated with a thin Au-Pd layer to reach proper conductivity and to avoid overcharging.

Results and discussion

The hybrid resin composites behaved tougher compared to the neat resin ones (Fig 2). In the interlaminar segment, hybrid resin matrix composites had higher shear strength values besides moderate standard deviations. Usefulness of composite materials can be characterized by their interlaminar properties because it refers to the quality of the matrix-reinforcement connection and toughness of the matrix material, as well.

Test of specimens loaded in fibre direction (0°) (Fig. 2/a) can provide information on the fibre-matrix connection, and its behaviour under shear stress. In case of the test of specimens loaded at 0°, EP/VE hybrid (regardless if made with method A or B) as matrix resulted in the best strength, higher than that of neat EP as matrix material. In case of EP/UP hybrid matrix, shear strength values were about the same as that of EP. Therefore it can be concluded that it is possible to create a good matrix from EP in a cost-efficient way because of the lower expense of UP component.

Test of specimens loaded perpendicularly (90°) to the reinforcement direction, can give important information about the properties of matrix, especially its toughness. In case of the test of specimens loaded at 90° to the reinforcement, the embedded fibre content can act like failure start points, from where crack propagation could proceed. According to results of 90° ILSS tests (Fig. 2/b), hybrid matrices behaved tougher compared to neat resins. The only exception was EP/UP hybrid made with method A, which had lower values than UP and EP as well. The observed increase in the properties can be traced back to the spatial phase structure of the mixed resins that indicate a proper connection between components in the mixed resin and on the matrix-reinforcement phase boundary, as well.

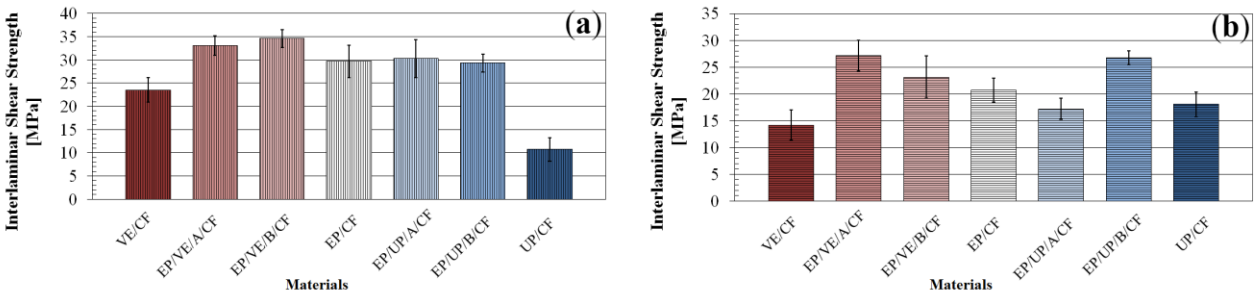

Figure 2 Interlaminar shear strength of the investigated composites in case of 0° (a) and 90° reinforcement (b) direction compared to loading

SEM pictures of the fracture surface of ILSS specimens loaded at 0° compared to reinforcement direction (Fig. 3) shows that the compatibility of the reinforcement and the matrix was proper in case of all investigated materials, but cracking mechanisms were different. Neat resin matrix ones, VE (Fig. 3/a), EP (Fig. 3/d), UP (Fig. 3/g) composites showed typical fracture surfaces with relatively proper level of adhesion. VE composite had tougher fracture, but had worse adhesion compared to the surface of EP composite. UP matrix composite was the worst from the toughness point of view and it had absolutely rigidly fractured surface. Hybrid matrix composites (Fig. 3/b, c, e, f) had

relatively good reinforcement-matrix connection, and had higher level of toughness compared to the neat matrix ones. Their fracture surface is partitioned, shell-like formations can be observed on them. Designation of the showed formations is hackle pattern [10, 11]. This phenomenon, which demanded more energy during the cracking process, was the reason for the higher level of interlaminar shear strength in case of hybrid resin matrix composites. The great increase in case of the EP/UP hybrids, compared to UP can root in larger lateral size of tough torn-fractured matrix surface (Fig. 3/b, c, e, f). The described fracture mechanism of mixed resin matrix composites could be explained by the micro- or nanostructured phase boundary system of the hybrid resins. Presumed entanglements in molecule chains and chain bands resulted in a tougher matrix, and may generate a better and tougher connection between the matrix and fibre reinforcement.

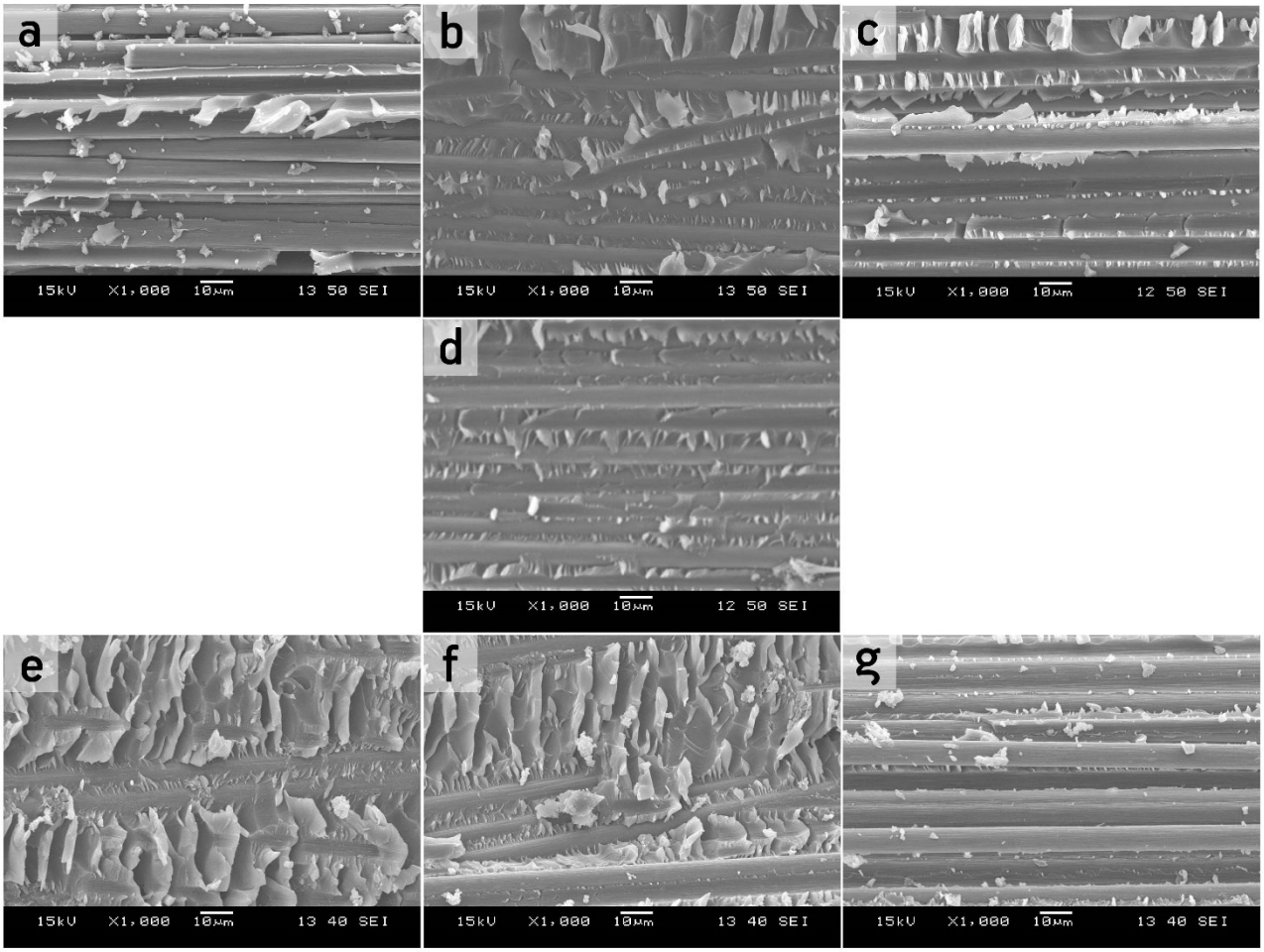

Figure 3 SEM micrographs of the fracture surface of ILSS specimens (loaded in the same direction as reinforcement orientation), VE/CF (a), EP/VE/A/CF (b), EP/VE/B/CF (c) EP/CF (d), EP/UP/A/CF (e), EP/UP/B/CF (f) and UP/CF (g)

Conclusions

In this study, high performance hybrid matrix carbon fibre reinforced composites were produced, and their mechanical properties were characterized by interlaminar shear tests. The fracture surfaces of composite specimens were investigated by scanning electron microscopy (SEM). According to the results, hybrid matrix composites had higher values of interlaminar shear strength, and were better in the field of toughness. These results were supported by SEM pictures that showed tougher crack propagation. The increase of shear strength, and this way toughness, could be explained by the phase structure of mixed resins. Another benefit of the hybrid resin systems, besides the improvement of mechanical properties, is their reduced cost compared to neat epoxy and their lower styrene content compared to initial VE and UP systems.

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